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(54) Low temperature process for depositing oxide layers by photochemical vapor deposition.

(57) The specification discloses a low temperature process for depositing oxide layers on a substrate by photochemical vapor deposition, by exposing the substrate to a selected vapor phase reactant in the presence of photo-chemically generated neutral (un-ionized) oxygen atoms. The oxygen atoms react with the vapor phase reactant to form the desired oxide, which deposits as a layer on the substrate. The use of photochemically generated neutral oxygen atoms avoids damage to the substrate due to charge bombardment or radiation bombardment of the substrate. The deposited oxide layer may optionally incorporate a selected dopant material in order to modify the physical, electrical, or optical characteristics of the oxide layer.

**EP 0 030 798 A1**

LOW TEMPERATURE PROCESS FOR  
DEPOSITING OXIDE LAYERS BY  
PHOTOCHEMICAL VAPOR DEPOSITION

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TECHNICAL FIELD

This invention relates generally to the manufacture of semiconductor devices and, more particularly, to a photochemical vapor deposition process for forming a dielectric oxide layer on the surface of a selected semiconductor material or an optical substrate, using a low temperature and non-ionizing radiation.

BACKGROUND ART

10 In the manufacture of semiconductor devices, it is frequently necessary to form a dielectric layer either as a passivation layer to permanently protect the surface of the substrate or as a mask during such procedures as etching, solid state diffusion, or ion-implantation.

15 One method by which an oxide layer, such as silicon dioxide ( $\text{SiO}_2$ ), may be formed is a plasma-enhanced chemical vapor deposition process as described by James A. Amick, G. L. Schnable, and J. L. Vossen, in the publication entitled, "Deposition Techniques for Dielectric Films or Semiconductor Devices," in the

20 Journal of Vacuum Science Technology, Vol. 14, No. 5, Sept.-Oct. 1977, pp. 1053-1063. In such a plasma-enhanced process, the vapor phase reactants, such as silane ( $\text{SiH}_4$ ) and nitrous oxide ( $\text{N}_2\text{O}$ ), are subjected to a radio frequency discharge, which creates an

25 ionized plasma of the reactant gases. These ionized reactants then interact to form the desired reaction

1 product. However, as a result of the exposure of the  
reactant gases to the radio frequency discharge, numerous  
extraneous ionized and neutral particles, as well as high  
energy radiation with wavelengths as low as 500 angstroms  
5 (Å) and even extending into the x-ray region, are pro-  
duced and bombard the surface of the substrate on which  
the oxide is being formed. If the substrate comprises  
a sensitive device type, such as a charge coupled device  
or a device formed of certain compound semiconductors  
10 (e.g., InSb, HgCdTe, or GaAs), the above-described charged  
particles and unwanted radiation frequently impart damage  
to these sensitive devices. For example, the deposited  
oxide layer may incorporate charges or dangling bonds,  
which create high surface state densities ( $N_{ss}$ ) at the  
15 semiconductor device/oxide layer interface and which  
will trap charges when a voltage is applied to the device,  
thereby preventing optimum device performance. In  
addition, a plasma enhanced deposition process has the  
disadvantage that plasma-induced heating of the substrate  
20 occurs as a result of selective absorption of the radio  
frequency energy by the substrate, and this heating causes  
uncertainty in the temperature of the substrate, which  
prevents optimization of the characteristics of the  
deposited oxide layer.

25 Other methods by which oxide layers may be formed  
use a non-reactive or a reactive sputtering technique.  
By a non-reactive sputtering technique, as described,  
for example, by Amick et al as referenced above, a disk  
of the selected oxide material, such as  $\text{SiO}_2$ , is bom-  
30 barded with argon ions, which cause the  $\text{SiO}_2$  to vaporize,  
and the vaporized  $\text{SiO}_2$  subsequently deposits on the selec-  
ted substrate. By a reactive sputtering technique, as  
described, for example, by Amick et al as referenced above,  
a disk of silicon is bombarded with oxygen ions, which  
causes vaporization of the silicon, and the vaporized  
35 silicon and oxygen ions then react to produce the desired

1 SiO<sub>2</sub>. However, these sputtering techniques are similar  
to the above-described plasma processes in that they fre-  
quently impart damage to sensitive devices due to charge  
bombardment or radiation bombardment of the device. In  
5 addition, the films produced by sputtering techniques  
are often granular, not dense, and not specular (i.e.,  
having good light reflecting properties).

Both the sputtering technique and the plasma-  
enhanced method for chemical vapor deposition may be  
10 used to deposit a dielectric layer which incorporates  
a selected dopant material. In the former case, an  
appropriately doped target could be bombarded by  
selected ions. In the latter case, a dopant-containing  
material is added to the reactant gases which are then  
15 ionized. However, both the above sputtering technique  
and the above plasma-enhanced method suffer from the  
difficulties discussed above, particularly that of  
imparting damage due to charge bombardment or radiation  
bombardment and plasma-induced heating of the substrate.

20 Still another method by which oxide layers may be  
formed involves thermal processes as described by  
Amick et al as referenced above. In order to form SiO<sub>2</sub>,  
for example, by a thermal process, silane is brought  
into contact with oxygen at a low temperature and a  
25 spontaneous reaction occurs, forming SiO<sub>2</sub>. The films  
formed by thermal processes, however, are usually granu-  
lar, do not necessarily have good adhesion, and tend  
to incorporate traps.

It is the alleviation of the prior art problem  
30 of imparting damage to sensitive devices due to charge  
bombardment or radiation bombardment during the formation  
of an oxide layer thereon to which the present invention  
is directed.

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SUMMARY OF THE INVENTION

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The general purpose of this invention is to provide a new and improved process for depositing a layer of an oxide of a chosen material on the surface of a selected substrate by low-temperature photochemical vapor deposition. This process possesses most, if not all, of the advantages of the above prior art oxide deposition processes, while overcoming their above-mentioned significant disadvantages.

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The above general purpose of this invention is accomplished by exposing the substrate to a selected vapor phase reactant in the presence of photochemically generated, neutral (unionized) oxygen atoms. The oxygen atoms react with the vapor phase reactant to form the desired oxide, which deposits as a layer on the substrate. The use of photochemically generated neutral oxygen atoms avoids damage to the substrate due to charge bombardment or radiation bombardment.

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Accordingly, it is an object of the present invention to provide a new and improved process for depositing a layer of an oxide of a chosen material on the surface of a selected substrate by a novel, low-temperature chemical vapor deposition process which avoids damage to the substrate from charge- or radiation-bombardment.

30

Another object of the present invention is to provide a process of the type described which minimizes the value of the surface state density at the oxide/semiconductor substrate interface and thus minimizes the charge traps in the deposited oxide layer.

35

Still another object is to provide a process of the type described which produces a low density of generation/recombination centers in the deposited oxide layer, and thus provides good minority carrier lifetime and reduced susceptibility to radiation damage in the device formed by this process.

BAD ORIGINAL



1 Another object is to provide a process of the type  
described which is performed at a temperature as low as  
room temperature (e.g. 30°C) and thus eliminates the  
problems of boundary migration and the resulting decreased  
5 device yields which are encountered in the fabrication  
of high density/high speed devices at higher temperatures.

Yet another object of the present invention is to  
provide a process of the type described which produces  
dense, non-granular, adherent oxide films on selected  
10 substrates.

Another object of the present invention is to  
provide a new and improved process for depositing a  
layer of a chosen oxide containing a selected dopant  
material on the surface of a substrate by a chemical  
15 vapor deposition process which avoids damage to the sub-  
strate due to charge bombardment or radiation bombardment.

Still another object is to provide a new and  
improved process for depositing a layer of a chosen oxide  
containing a selected dopant material on the surface  
20 of a substrate, which uses a photochemical technique.

The foregoing and other objects, features, and  
advantages of the present invention will be apparent  
from the following more particular description of the  
preferred embodiments of the invention, as illustrated  
25 in the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates, in schematic form, a preferred  
apparatus for carrying out the processes according to  
30 first and second embodiments of the present invention,  
in which neutral oxygen atoms are formed by the mercury  
photosensitized dissociation of an oxygen-containing  
precursor and are reacted to form an undoped or a doped  
oxide layer, respectively.

35 FIG. 2 illustrates, in schematic form, a preferred  
apparatus for carrying out the processes according to

1 third and fourth embodiments of the present invention,  
in which neutral oxygen atoms are formed by the direct  
dissociation of an oxygen-containing precursor and are  
reacted to form an undoped or a doped oxide layer,  
5 respectively.

#### DETAILED DESCRIPTION OF THE INVENTION

FIG. 1 shows, in simplified form, an apparatus suitable  
for implementation of two process embodiments of the present  
10 invention in which neutral oxygen atoms are formed by the  
mercury photosensitized dissociation of a chemically  
unreactive oxygen-containing precursor, such as nitrous  
oxide ( $N_2O$ ), molecular oxygen ( $O_2$ ), or nitrogen dioxide  
( $NO_2$ ). (The term "chemically unreactive" is used herein  
15 to denote that a substance will not react with the  
designated reactants under normal mixture conditions.)  
A reaction chamber 10, in which the chemical vapor depo-  
sition reaction occurs, is provided with a quartz window  
12, which is integral with the top surface of the reaction  
20 chamber 10. The quartz window 12 is transmissive to the  
selected wavelength of radiation used to initiate the  
desired photochemical reaction to be discussed below,  
and this radiation 14 of a selected wavelength is produced  
by the radiation-producing means 16, which may be, for  
25 example, an array of low pressure mercury vapor arc lamps.  
Within the reaction chamber 10, there is a substrate  
holder 18, which receives a substrate 20 onto which the  
desired oxide layer is to be deposited.

External to the reaction chamber 10 and adjacent to  
30 the bottom surface thereof, there are heating elements  
21, which may be formed, for example, of Nichrome wire  
and are activated by applying a controlled voltage  
thereto. The heating elements 21 may be used optionally  
to heat the substrate 20 to the required temperature  
35 so that appropriate properties of the deposited layer,  
such as density, may be obtained. The temperature in

1 the chamber 10 may be maintained as low as room temper-  
ature (i.e. 30°C) or as high as required (e.g., 300°C  
or higher). However, since mercury vapor arc lamps, for  
example, become less efficient at increased temperatures,  
5 it is necessary to provide external water cooling or an  
external air or nitrogen cooling source to cool these  
lamps and remove radiant heat produced by the substrate 20  
and substrate holder 18 at certain elevated temperatures  
(as high as 600°C, for example, or higher). For this  
10 purpose, the radiation-producing means 16 is completely  
contained within the enclosure 23, which may be formed  
of aluminum, and an external cooling means 25, such as  
pipes with water flowing therethrough as shown in FIG. 1  
or flowing nitrogen gas, is activated to apply cooling  
15 to the enclosure 23. The enclosure 23 is secured to the  
outside surface of the reaction chamber 10 which surrounds  
the quartz window 12, but may be removed therefrom as  
required. Thus, the processing temperature is maintained  
at a level such that sufficient cooling of the mercury  
20 lamps can be accomplished in order to provide efficient  
lamp performance. The enclosure 23 also provides eye  
protection to the operator from the radiation 14. Leading  
from the reaction chamber 10, there is a tube 22 which  
passes through a valve 24 and then to a vacuum-producing  
25 means, such as a pump, (not shown), which is used to  
evacuate the chamber 10 to a sufficiently low pressure  
to allow the vapor deposition reaction to occur.

External to the reaction chamber 10, there are cham-  
30 bers 26 and 28 which contain the individual reactant gases  
for the selected chemical vapor deposition reaction, for  
example, silane and nitrous oxide. The chambers 26 and  
28 are connected to control valves or flowmeters 30 and  
32, respectively, which are used to control the amounts  
of reactants which are introduced into a tube 34. Alter-  
35 natively, for a second process embodiment of the present  
invention (discussed below), there are included a third



1 chamber 27, which contains the precursor of the selected  
dopant material, such as phosphine, and a corresponding  
control valve or flowmeter 31, which controls the amount  
of dopant precursor introduced from the chamber 27 into  
5 the tube 34, where it is mixed with the other reactant  
gases discussed above.

The reactant gases flow through the tube 34 into a  
chamber 36 which contains a pool of mercury (at room  
temperature) having mercury vapor above it, at a vapor  
10 pressure of  $10^{-3}$  Torr at 30°C. The reactant gases thus  
become mixed with mercury vapor in the chamber 36 and  
this reactant gas mixture then passes through a tube 38  
and into the reaction chamber 10, where the chemical vapor  
deposition reaction may be brought about. The components  
15 of the apparatus shown in FIG. 1 may be constructed of  
stainless steel or aluminum, unless otherwise specified.  
The apparatus shown in FIG. 1 may be used for either  
a low pressure continuous flow photochemical reactor  
system, in which there is a continuous influx of reactant  
20 gases and removal of reaction by-products during the  
photochemical reaction process, or for a static photo-  
chemical reactor system, in which specified amounts of  
reactants are introduced into the reaction chamber, the  
flow of reactant gases is stopped, and then the photo-  
25 chemical reaction process is allowed to occur.

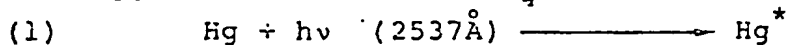
In practicing the present invention in accordance  
with the first embodiment thereof, which depends on the  
photochemical generation of atomic oxygen, and using the  
apparatus of FIG. 1 with only two reactant gas chambers  
30 (chambers 26 and 28), a chemical vapor deposition process  
is performed as generally described by Werner Kern and  
Richard S. Rosler in the publication entitled, "Advances  
in Deposition Processes for Passivation Films", in the  
Journal of Vacuum Science Technology, Vol. 14, No. 5,  
35 Sept.-Oct. 1977, pp. 1082-1099, in the discussion of  
low pressure chemical vapor deposition processes. The

1 reaction chamber 10 is evacuated by the vacuum-producing  
means to a predetermined pressure, for example 1 to 4 Torr.  
The selected vapor phase reactant, such as  $\text{SiH}_4$ , is placed  
in a chamber such as the chamber 26, and a chemically  
5 unreactive oxygen-containing precursor, such as  $\text{N}_2\text{O}$ , is  
placed in a chamber such as the chamber 28. The valves 30  
and 32 are set so that the reactants from the chambers 26  
and 28, respectively, in a predetermined ratio and at a  
predetermined flow rate may pass into the tube 34 and then  
10 into the chamber 36, which contains a pool of mercury.  
These reactant gases become mixed with mercury vapor in the  
chamber 36 and pass from the chamber 36 through the tube  
38 into the reaction chamber 10, which is maintained at  
approximately room temperature (e.g.  $30^\circ\text{C}$ ) or up to  $200^\circ\text{C}$   
15 or higher. The radiation-producing means 16 is activated  
and produces the radiation 14 of a selected wavelength  
required to produce the desired photochemical reaction  
(e.g.  $2537\text{\AA}$  to produce mercury in an excited state). The  
radiation 14 passes through the quartz window 12 into the  
20 reaction chamber 10, where it excites the mercury (Hg)  
atoms in the reactant gas mixture to form mercury atoms  
in an excited state ( $\text{Hg}^*$ ) (approximately 5 electron volts  
above normal ground state, but unionized), as shown in  
Equation (1) below. The  $\text{Hg}^*$  then collides with the oxygen-  
25 containing precursor, such as  $\text{N}_2\text{O}$ , and causes the precursor  
to dissociate and produce atomic oxygen (O), as shown in  
Equation (2a) below.

In addition, the  $\text{Hg}^*$  may react with the selected  
vapor phase reactant, such as  $\text{SiH}_4$ , to produce a  
30 reactive radical, such as  $\cdot\text{SiH}_3$ , as shown in equation  
(2b) below. Finally, the atomic oxygen reacts with the  
reactant,  $\text{SiH}_4$ , or the reactive radical, such as  $\cdot\text{SiH}_3$ ,  
to produce the desired oxide, such as  $\text{SiO}$  and  $\text{SiO}_2$ , as  
shown in Equations (3a) and (3b) below. Either  $\text{SiO}$  or  
35  $\text{SiO}_2$  can be produced, depending on the reactant gas ratio

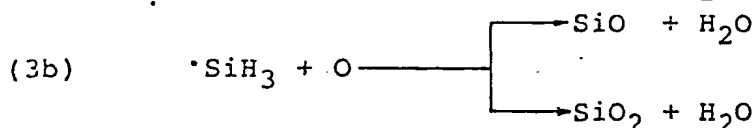
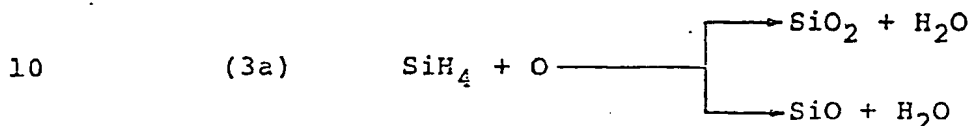
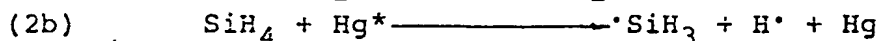
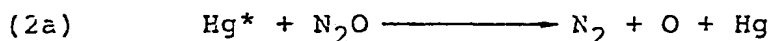


1 of  $\text{SiH}_4$  and  $\text{N}_2\text{O}$  (i.e. the steady state concentration of atomic oxygen which oxidizes  $\text{SiH}_4$ ).



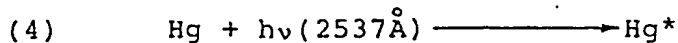
where  $h$  = Planck's constant

$\nu$  = frequency of absorbed radiation



15 The reaction of  $\text{Hg}^*$  with  $\text{SiH}_4$  to form the radical  $\cdot\text{SiH}_3$  is a side reaction which is not necessary to the process of the present invention, but leads to the same end product as the major reaction path. The atomic oxygen produced in Equation (2a) above may react directly with the selected vapor phase reactant without first forming an intermediate radical, as described in Equation (3a) above.

Alternatively, the atomic oxygen required for this first process embodiment of the present invention may be formed by the mercury sensitized dissociation of nitrogen dioxide ( $\text{NO}_2$ ) to form atomic oxygen and  $\text{NO}$ . Further, atomic oxygen may also be formed by the mercury sensitized dissociation of molecular oxygen in accordance with Equations (4) and (5) below, or by other known means for forming atomic oxygen by photochemical processes.



Since molecular oxygen reacts spontaneously with  $\text{SiH}_4$  as discussed in relation to the prior art thermal oxidation process, it is necessary to inhibit this spontaneous thermal oxidation process in order to permit

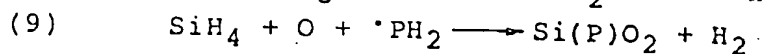
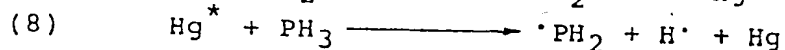
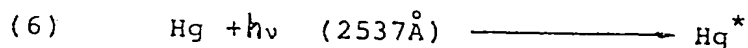
1 the formation of atomic oxygen and the reaction thereof  
with  $\text{SiH}_4$  in accordance with the process of the present  
invention. This inhibition is accomplished by carefully  
controlling the operating pressure and the ratio of  
5 reactant gases, as discussed in more detail in Example 3  
below. By controlling such process parameters the thermal  
oxidation process may be completely inhibited and  
the oxidation process of the present invention may occur  
without any competing processes.

10 By the above-described process of the present  
invention, oxygen atoms are produced by a photochemical  
process which generates only neutral particles. Thus,  
the prior art problems associated with the generation  
of charged particles and high energy radiation which  
15 bombard the substrate have been avoided. The value  
of the surface state density ( $N_{ss}$ ) at the oxide/semi-  
conductor substrate interface and thus the charge  
traps in the oxide or insulator layer are minimized by  
the process of the present invention. In addition, a low  
20 density of generation/recombination centers (i.e., dang-  
ling bonds or traps) is produced and thus good minority  
carrier lifetime is achieved in devices formed by the  
process of the present invention. In addition, the  
process of the present invention provides enhanced pro-  
25 tection against device damage due to radiation (i.e.  
from a cobalt-60 source) by minimizing the creation of  
dangling bonds and traps during the deposition of the oxide  
or insulator layer. These traps and dangling bonds nor-  
mally increase the probability of radiation damage to  
30 the device and their minimization thus ~~minimizes the~~ <sup>reduces the probability of</sup>  
radiation damage. Further, the problem of boundary  
migration has been eliminated since the process of the  
present invention can be conducted at a relatively low  
temperature, i.e. as low as room temperature, and the  
35 associated problem of decreased device yield encountered  
in the high temperature fabrication of high density

1 devices such as very large scale integrated circuits and  
very high speed integrated circuits, has been avoided.  
In addition, the prior art problem of plasma-induced  
heating is avoided by the process of the present invention  
5 since selective absorption of radiation by the substrate  
does not occur in the process described herein. Further-  
more, the process of the present invention is free of  
particulate formation, for example, on chamber walls,  
which is a problem often encountered in the prior art  
10 processes discussed above. Finally, the oxide layer  
formed by the process of the present invention is dense,  
non-granular, scratch-resistant, specular, has negligible  
porosity, and is strongly adherent to a variety of sur-  
faces, such as semiconductor, metal and inorganic sur-  
15 faces. Such oxide layers find utility both as a passi-  
vation layer and as a gate insulator layer in integrated  
circuit devices. Furthermore, these oxide layers may  
be used as a conformal coating on integrated circuits  
and hybrid microcircuits. In addition, these oxide  
20 layers may be used in the fabrication of HgCdTe photo-  
conductive and photovoltaic devices. This first process  
embodiment of the present invention and the related third  
process embodiment discussed below are, to my knowledge,  
the first demonstration of the use of a photochemical  
25 process for the deposition of a dielectric layer on a  
substrate.

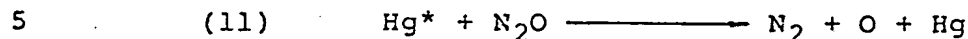
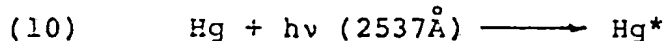
Using the above-described process, the present  
invention may also be used to oxidize trimethyl aluminum,  
(CH<sub>3</sub>)<sub>3</sub> Al, to Al<sub>2</sub>O<sub>3</sub>; trimethyl gallium, (CH<sub>3</sub>)<sub>3</sub> Ga, to  
30 Ga<sub>2</sub>O<sub>3</sub>; germane, GeH<sub>4</sub>, to GeO<sub>2</sub>; diborane, B<sub>2</sub>H<sub>6</sub>, to B<sub>2</sub>O<sub>3</sub>;  
trimethyl indium, (CH<sub>3</sub>)<sub>3</sub> In to In<sub>2</sub>O<sub>3</sub>; titanium tetra-  
chloride, TiCl<sub>4</sub>, to TiO<sub>2</sub>; tungsten hexafluoride, WF<sub>6</sub>,  
to W<sub>2</sub>O<sub>3</sub>, and hafnium hydride, HfH<sub>4</sub>, to HfO<sub>2</sub>. This first  
process embodiment of the present invention is illustrated  
35 in Example 1 below.

1 Furthermore, a process carried out in accordance  
 with a second embodiment of the present invention may be  
 performed by practicing the present invention as described  
 above, using the apparatus of FIG. 1 with three (3)  
 5 reactant gas chambers (chambers 26, 27, and 28), to deposit  
 on the surface of a chosen substrate an oxide layer which  
 incorporates a selected dopant material in order to  
 modify the physical, electrical, or optical character-  
 10 istics of the oxide layer. To accomplish this second  
 process embodiment of the present invention, the selected  
 vapor phase reactant, such as  $\text{SiH}_4$ , is exposed to simul-  
 taneously formed and photochemically generated neutral  
 oxygen atoms and neutral atoms or atomic fragments of  
 15 the selected dopant, such as phosphorus - containing  
 phosphinyl radicals. The neutral atomic particles are  
 produced by the mercury photosensitized dissociation  
 of a chemically unreactive oxygen-containing precursor,  
 such as nitrous oxide ( $\text{N}_2\text{O}$ ) and a chemically unreactive  
 20 dopant-containing precursor, such as phosphine ( $\text{PH}_3$ ),  
 which results in the generation of atomic oxygen and  
 neutral phosphinyl radicals, respectively, as shown  
 in Equations (6) through (8) below. The atomic oxygen  
 and phosphinyl radicals subsequently oxidize the  $\text{SiH}_4$   
 to phosphorus-doped silicon dioxide [ $\text{Si(P)O}_2$ ], as  
 25 shown in Equation (9) below.



30 A mechanistic alternative to the sequence described  
 above involves the simultaneous oxidation of both  $\text{SiH}_4$  and  
 $\text{PH}_3$  by atomic oxygen, as indicated in Equations (10)  
 through (12) below. Thus, atomic oxygen alone may be suf-  
 ficient to bring about the desired reaction as shown in  
 35 Equation (12) below. Consequently, the production of neu-  
 tral particles of the selected dopant material as described

1 above in Equation (8) may not be necessary in practicing  
the second process embodiment of this invention, but  
may occur.



The procedure followed to accomplish this second  
process embodiment of the invention is essentially as  
described above with respect to the first process embodi-  
10 ment of the present invention, except that additionally,  
a controlled amount of a selected dopant-containing pre-  
cursor is introduced from the chamber 27 through the  
control valve 31 into the tube 34, where it mixes with  
the reactant gases from the chambers 26 and 28.

15 Thus, by this second process embodiment of the pre-  
sent invention, a doped dielectric film may be deposited  
by a low-temperature process which avoids the generation  
of charged particles and high energy radiation and their  
consequent bombardment damage to the substrate. Addition-  
20 ally, this embodiment has all the advantages enumerated  
above with respect to the formation of an undoped  
dielectric layer by the process of the present invention.  
This second process embodiment of the present invention  
and the related fourth process embodiment discussed below  
25 are, to my knowledge, the first demonstration of the  
use of a photochemical process for the deposition of  
a doped dielectric layer.

By the process according to this second embodiment  
of the present invention, other dopants besides phosphorus  
30 may be incorporated in the deposited dielectric layer by  
addition of the corresponding dopant-containing precursor  
to the reactant gas mixture. For example, diborane ( $\text{B}_2\text{H}_6$ )  
may be used for boron doping, arsine ( $\text{AsH}_3$ ) may be used for  
arsenic doping, stibine ( $\text{SbH}_3$ ) may be used for antimony  
35 doping, hydrogen selenide ( $\text{H}_2\text{Se}$ ) may be used for selenium  
doping, hydrogen sulfide ( $\text{H}_2\text{S}$ ) may be used for sulfur

1 doping, or hydrogen telluride ( $H_2Te$ ) may be used for  
tellurium doping. Other dopant-containing precursors  
which are capable of the mercury photosensitized  
dissociation reaction of the type discussed herein may  
5 also be used. Other dielectric films besides  $SiO_2$  may  
be formed, as discussed above. This second process embodi-  
ment of the present invention is illustrated in more  
detail in Example 2 below.

Turning now to FIG. 2, there is shown an apparatus  
10 suitable for implementation of the processes according to  
of third and fourth embodiments of the present invention,  
in which neutral oxygen atoms are formed by a direct  
photochemical reaction of an oxygen-containing precursor,  
thus eliminating the requirement of mercury photosensitiza-  
15 tion. A reaction chamber 40 in which the photochemical  
vapor deposition reaction occurs is provided with a trans-  
parent window 42, which is integral with the top surface  
of the chamber 40. The material of which the window 42  
is formed is chosen to be transparent to the selected  
20 wavelength of radiation which will be used for the photo-  
chemical reaction. Radiation 44 having a selected  
wavelength is produced by a radiation-producing means  
46, such as an array of low pressure mercury vapor arc  
lamps, and passes through the window 42 into the chamber  
25 40. Within the reaction chamber 40, there is a substrate  
holder 48, which holds a substrate 50 onto which the  
desired oxide layer is to be deposited. External to the  
reaction chamber 40 at the bottom surface thereof, there  
are heating elements 51, which may be formed of Nichrome  
30 wire and are activated by application of a controlled  
voltage thereto. The heating elements 51 may be used  
optionally to preheat the substrate 50 to the required  
temperature for forming a deposited layer with desired  
properties.





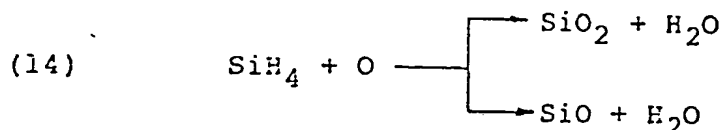
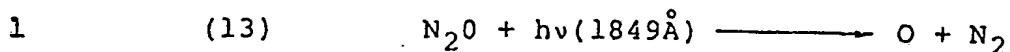
1           In practicing the present invention, the temperature  
in the chamber 40 may be maintained as low as room tempera-  
ture or as high as 200°C or higher. In order to provide  
the required cooling of the radiation-producing means 46,  
5   as previously discussed in relation to FIG. 1, radiation-  
producing means 46 is completely enclosed within the  
enclosure 53, which may be formed of aluminum, and an  
external cooling means 55, such as pipes with water flow-  
ing therethrough as shown in FIG. 2 or flowing nitrogen  
10 gas, is activated to apply cooling to the enclosure 53.  
The enclosure 53 performs the additional function of  
eliminating the formation of ozone which would occur if  
the radiation 44 (such as 1849 Å radiation) were allowed  
to contact molecular oxygen in the open atmosphere,  
15 which would cause the formation of atomic oxygen that  
would then react with additional molecular oxygen in  
the atmosphere to form ozone. The enclosure 53 is  
secured to the outside surface of the reaction chamber  
40 which surrounds the quartz window 42, but may be  
20 removed therefrom as required.

Leading from the reaction chamber 40, there is a  
tube 52 which passes through a valve 54 and then to a  
vacuum producing means, e.g., a vacuum pump, (not shown)  
which is used to evacuate the chamber 40 to a sufficiently  
25 low pressure (e.g., 1-4 Torr) to allow the vapor deposition  
reaction to occur.

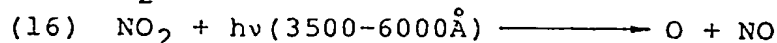
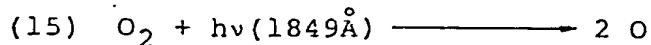
External to the reaction chamber 40, there are  
chambers 56 and 58, which contain the individual selected  
reactant gases, such as silane ( $\text{SiH}_4$ ) and nitrous oxide  
30 ( $\text{N}_2\text{O}$ ), respectively, for producing the desired photo-  
chemical reaction. The chambers 56 and 58 are connected  
to control valves or flowmeters 60 and 62, respectively,  
which are used to control the amounts of reactants which  
are introduced into a tube 64. Alternatively, in accord-  
35 ance with a fourth process embodiment of the present  
invention (discussed below), there are included a third

1 chamber 57, which contains the precursor of the selected  
dopant material, such as phosphine, and a corresponding  
control valve or flowmeter 61, which controls the amount  
5 of dopant precursor introduced from the chamber 57 into  
the tube 64, where it is mixed with the other reactant  
gases discussed above. The reactant gases flow through  
the tube 64 into the reaction chamber 40, where the  
photochemical reaction may be brought about. The compo-  
nents of the apparatus shown in FIG. 2 may be constructed  
10 of stainless steel or aluminum, unless otherwise speci-  
fied. The apparatus shown in FIG. 2 may be used for  
either a continuous flow photochemical reactor system  
or a static photochemical reactor system, as discussed  
above with reference to FIG. 1.

15 In practicing the present invention in accordance  
with the third embodiment thereof and using the apparatus  
of FIG. 2, the general process described in relation  
to the first process embodiment of FIG. 1 is followed,  
except that no mercury is used for photosensitization.  
20 The valves 60 and 62 are set so that the reactant gases,  
such as  $\text{SiH}_4$  and  $\text{N}_2\text{O}$ , from the chambers 56 and 58,  
respectively, pass in a predetermined ratio and at a  
predetermined flow rate into the tube 64 and then into  
the reaction chamber 40. The radiation-producing means 46  
25 is activated and produces the radiation 44 of a selected  
wavelength, which is the appropriate wavelength to cause  
the direct dissociation of the selected oxygen-containing  
precursor (e.g. 1750-1950 $\text{\AA}$  for  $\text{N}_2\text{O}$ ). The radiation 44  
passes through the window 42, which is formed of a mate-  
30 rial that is transparent to the wavelength of the radia-  
tion 44. The radiation 44 passes into the reaction cham-  
ber 40, where it causes the dissociation of the selected  
oxygen-containing precursor, such as  $\text{N}_2\text{O}$ , into atomic  
oxygen, which then reacts with the selected vapor phase  
35 reactant, such as  $\text{SiH}_4$ , to form the desired oxide, such as  
 $\text{SiO}_2$  and  $\text{SiO}$ , as shown in Equations (13) and (14) below.



5           Alternatively, the atomic oxygen required for this  
third process embodiment of the present invention may  
be formed by the direct photochemical dissociation of  
molecular oxygen as shown in Equation (15) below or of  
nitrogen dioxide ( $\text{NO}_2$ ) as shown in Equation (16) below  
10 or of similar known materials which are capable of  
dissociation to oxygen by a direct photochemical process.



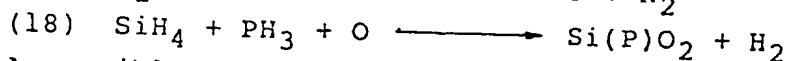
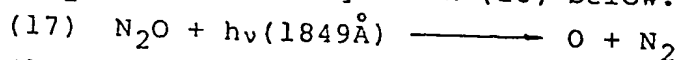
When molecular oxygen is used as the source of atomic  
15 oxygen, the operating pressure and reactant gas ratio  
must be carefully controlled in order to inhibit the  
spontaneous thermal oxidation of the  $\text{SiH}_4$  by the  $\text{O}_2$ ,  
as previously discussed in relation to an alternative  
process embodiment of the present invention and as  
20 illustrated in Example 3 below.

By the above-described process in accordance with  
this third embodiment of the present invention, oxygen  
atoms are generated by a photochemical process which  
produces only neutral particles. Thus, the previously  
25 discussed prior art problems caused by the generation  
of charged particles and high energy radiation and their  
bombardment of the substrate have been avoided. The  
advantages of this third process embodiment of the present  
invention are the same as those discussed in relation  
30 to the first process embodiment described with respect  
to FIG. 1. In addition, the process according to this  
third embodiment has the advantage that no photosensitizing  
mercury is necessary, and thus possible mercury contami-  
nation of the deposited oxide can be avoided. Further,  
35 the apparatus for carrying out the process according

1 to this third embodiment is less complex than an apparatus  
 requiring the use of mercury.

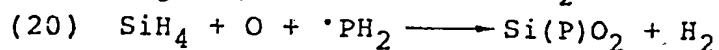
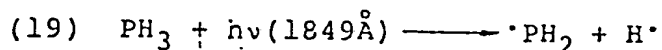
Using the above-described process, the present  
 invention may also be used to deposit dielectric oxides  
 5 of gallium, germanium, boron, and indium and metal oxides  
 of aluminum, tungsten, titanium, and hafnium, using the  
 gas phase reactants discussed in relation to FIG. 1.  
 This third process embodiment of the present invention  
 is illustrated in Example 3 below.

10 Furthermore, a process carried out in accordance  
 with a fourth embodiment of the present invention may  
 be performed by practicing the present invention as  
 described above, but also using the apparatus of FIG. 2  
 with three (3) reactant gas chambers (chambers 56, 57,  
 15 and 58), to deposit an oxide layer which incorporates  
 a selected dopant material, on the surface of a chosen  
 substrate. To accomplish this fourth process embodi-  
 ment of the present invention, the selected vapor phase  
 reactant, such as  $\text{SiH}_4$ , is exposed to photochemically  
 20 generated neutral oxygen atoms in the presence of a  
 dopant-containing precursor, such as phosphine ( $\text{PH}_3$ ).  
 The neutral atomic oxygen is produced by direct dissocia-  
 tion of an oxygen-containing precursor, such as  $\text{N}_2\text{O}$ ,  
 by radiation of a selected wavelength as shown in Equa-  
 25 tion (17) below. The atomic oxygen then simultaneously  
 oxidizes the  $\text{SiH}_4$  and  $\text{PH}_3$  to form the desired phosphorus-  
 doped  $\text{SiO}_2$  as shown in Equation (18) below.



30 A possible alternative to the above-described  
 sequence involves the direct dissociation of the dopant-  
 containing precursor such as phosphine to form a neutral  
 phosphinyl radical as shown in Equation (19) below. The  
 phosphinyl radical so formed and the atomic oxygen formed  
 35 in accordance with the direct dissociation reaction of  
 Equation (17) above then react with the silane reactant :

1 to form the desired phosphorus-doped  $\text{SiO}_2$  as shown in  
Equation (20) below.



5 The procedure followed to accomplish the process  
according to the fourth embodiment of this invention  
is essentially as described above with respect to the  
third process embodiment of the present invention, except  
that additionally a controlled amount of a selected  
10 dopant-containing precursor, such as phosphine gas, is  
introduced from the chamber 57 and through the valve 61  
into the tube 64, where it mixes with the reactant gases  
from the chambers 56 and 58.

Thus, by this fourth process embodiment of the  
15 present invention, a doped dielectric film may be  
deposited by a low-temperature process which avoids  
the generation of charged particles and high energy radia-  
tion and their consequent bombardment damage to the  
substrate and additionally avoids the use of mercury  
20 for photosensitization. The significance of these  
advantages has been discussed above with respect to  
the third process embodiment of the present invention.  
Various dopant materials other than phosphine may be  
used, and these materials include diborane, arsine,  
25 stibine, hydrogen selenide, hydrogen sulfide, hydrogen  
telluride, or other dopant-containing precursors which  
are capable of simultaneous oxidation by atomic oxygen  
with the selected gas phase reactant to form the desired  
doped oxide layer. This fourth process embodiment of  
30 the present invention is illustrated in Example 4 below.

#### EXAMPLE 1

This example illustrates the use of the process  
according to the first embodiment of the present inven-  
35 tion as previously described herein.

1        Using the apparatus described and illustrated in  
relation to FIG. 1 with two reactant gas chambers, SiO  
and SiO<sub>2</sub> were independently deposited on the surface  
of a wafer of silicon having a two-inch diameter. Nitrous  
5        oxide was used as the oxygen-containing precursor and  
silane was the selected vapor phase reactant. The reac-  
tion chamber 10 was evacuated by the vacuum-producing  
means to a pressure of 10<sup>-3</sup> Torr, then back-filled with  
nitrogen, and again evacuated to a pressure of 10<sup>-3</sup> Torr.  
10        The flowmeters 30 and 32 were activated to admit the  
reactant gases (SiH<sub>4</sub> and N<sub>2</sub>O) in a predetermined ratio  
into the tube 34 and subsequently into the chamber 36  
and the reaction chamber 10, and the reactant gas flow  
rates were stabilized. The operating pressure within the  
15        reaction chamber 10 was adjusted by means of the valve 24  
to achieve a pressure of approximately 1 Torr. The heat-  
ing elements 21 and the cooling means 25 were activated.  
Finally, the low pressure mercury arc resonance lamps  
were activated and emitted radiation at 2537Å, which  
20        was absorbed by the mercury vapor in the reaction  
chamber, producing photo-excited mercury atoms, which  
collided with the nitrous oxide to form atomic oxygen.  
The atomic oxygen then oxidized the silane to either  
SiO<sub>2</sub> or SiO. When using a continuous flow photochemical  
25        reactor system at an operating pressure of 2 Torr, with  
a reactant gas flow ratio of 2 standard cubic centimeters  
per minute (sccm) of SiH<sub>4</sub> to 50 sccm of N<sub>2</sub>O, a layer of  
SiO<sub>2</sub> was produced. When a reactant gas flow ratio of  
2 sccm of SiH<sub>4</sub> to 10 sccm of N<sub>2</sub>O was used in a continuous  
30        flow system, a layer of SiO was produced. At a substrate  
temperature of 100°C, the silicon oxide layer was deposi-  
ted at the rate of 200Å per minute using a continuous  
flow system. When using a static photochemical reactor  
system with a reactant gas ratio of SiH<sub>4</sub> to N<sub>2</sub>O of 3  
35        millimeters (mm) to 12 mm, silicon monoxide (SiO) was  
produced as a layer on the surface of the silicon wafer.

1 When a reactant gas ratio of  $\text{SiH}_4$  to  $\text{N}_2\text{O}$  of 3.0mm to 30mm  
was used in a static system, silicon dioxide ( $\text{SiO}_2$ )  
was produced as the layer on the silicon wafer.

5 The refractive index of the photodeposited silicon  
oxide layers formed by the process of this embodiment of  
the present invention was determined by ellipsometry  
as a function of the reactant gas mixture ratio,  $\text{N}_2\text{O}/\text{SiH}_4$ .  
Mixtures rich in  $\text{N}_2\text{O}$  (i.e. atomic oxygen) produced  
10 films with a refractive index characteristic of  $\text{SiO}_2$ ,  
i.e. 1.45. Mixtures of  $\text{N}_2\text{O}/\text{SiH}_4$  progressively leaner  
in  $\text{N}_2\text{O}$  yielded silicon oxide films with less oxygen  
content and, ultimately,  $\text{SiO}$  with a refractive index  
of 1.88. The etch rate characteristics of the photo-  
deposited  $\text{SiO}_2$  material in buffered HF were comparable  
15 to those of  $\text{SiO}_2$  films deposited by low temperature plasma  
techniques. The stoichiometric composition of the film  
was determined by Auger electron spectroscopy. The  $\text{SiO}_2$   
films exhibited an excellent composition/depth pro-  
file and stoichiometrically were equivalent to pure  
20  $\text{SiO}_2$ . The  $\text{SiO}$  films exhibited slower etch rates than  
the  $\text{SiO}_2$  films due to the depleted oxygen content of  
the  $\text{SiO}$  films, which was confirmed by Auger spectroscopic  
analysis. The breakdown voltage of the  $\text{SiO}_2$  films formed  
by the process of the present invention was determined  
25 to be  $3.0 \times 10^6$  volts/centimeter, the dielectric constant  
was approximately 5.5, and the dissipation factor was  
 $1.5 \times 10^{-2}$ , which measurements are comparable to the  
values obtained for similar films formed by a prior art  
thermal process previously discussed. The density of  
30 the  $\text{SiO}_2$  films formed by the process of the present  
invention was 2.3 grams/cubic centimeter.

The photochemically deposited  $\text{SiO}_2$  layers formed  
by the above-described process of the present invention  
have application as dielectric layers for the passivation  
35 of semiconductor devices, particularly charge-sensitive  
microelectronic devices, such as silicon MOS devices,



1 HgCdTe photoconductive and photovoltaic devices, and  
GaAs field-effect transistors. These layers may be  
deposited to a typical thickness of 1200-1500 $\text{\AA}$  for such  
a purpose. In addition, the process of the present inven-  
5 tion may be used to deposit an anti-reflective oxide  
coating on a lens, including a plastic lens, or a solar  
cell, or to deposit a protective oxide coating on a mirror.

Using the above-described process,  $\text{SiO}_2$  layers  
were similarly deposited on Ge, InSb, and Al substrates.

10

#### EXAMPLE 2

This example illustrates the use of the process  
according to the second embodiment of the present  
invention as previously described herein.

15 Using the apparatus described and illustrated in  
relation to FIG. 1 with three reactant gas chambers, a  
layer of phosphorus-doped  $\text{SiO}_2$  was deposited on the sur-  
face of a silicon wafer having a two-inch diameter. The  
general procedure described in relation to Example 1  
20 above was followed, with the addition of a third reactant  
gas. Nitrous oxide was used as the oxygen-containing  
precursor, silane was the selected vapor phase reactant,  
and phosphine was the phosphorus dopant-containing pre-  
cursor. The process was initiated by the photochemical  
25 excitation of mercury vapor at  $10^{-3}$  Torr in a quartz  
reaction chamber. Low pressure mercury arc resonance  
lamps emitted radiation at 2537 $\text{\AA}$ , which was absorbed  
by the mercury vapor in the reaction chamber, producing  
photo-excited mercury atoms that reacted with the  $\text{N}_2\text{O}$   
30 and  $\text{PH}_3$  as shown in Equations (7) and (8) discussed above.  
The atomic oxygen and neutral phosphinyl radical ( $\cdot\text{PH}_2$ )  
thus formed reacted with the  $\text{SiH}_4$  to form phosphorus-  
doped silicon dioxide  $[\text{Si}(\text{P})\text{O}_2]$  as shown in Equation  
(9) discussed above, which deposited as a layer on the  
35 silicon wafer. Using a continuous flow photochemical  
reactor system, with a reactant gas flow ratio of





1  $\text{SiH}_4/\text{N}_2\text{O}/\text{PH}_3$  of 2/60/1 sccm, a phosphorus-doped  $\text{SiO}_2$  layer was deposited on the substrate at the rate of  
200Å/minute and the phosphorus content of the deposited  
5 static photochemical reactor system was used with a reactant gas ratio of  $\text{SiH}_4/\text{N}_2\text{O}/\text{PH}_3$  of 3/30/1 mm. The phosphorus-doped  $\text{SiO}_2$  layer was deposited at initial rates of 200Å/minute and the phosphorus-content in the deposited layer was approximately 5%. Using a reactant  
10 gas ratio of  $\text{SiH}_4/\text{N}_2\text{O}/\text{PH}_3$  of 2/30/12 mm in a static system, levels of phosphorus-doping of 17% in the deposited layer have been achieved.

The refractive index of the photodeposited phosphorus-doped  $\text{SiO}_2$  layer was dependent on the  $\text{N}_2\text{O}/\text{PH}_3$   
15 ratio and indices from 1.55 to 1.65 were measured. The films exhibiting the higher refractive indices indicated a greater phosphorus doping content of the  $\text{SiO}_2$  dielectric material. The chemical composition of the phosphorus-doped  $\text{SiO}_2$  films was determined by Auger electron spectroscopy and the phosphorus content was confirmed by energy  
20 dispersive X-ray analysis (EDAX). The etch rate in "P-etch" [i.e., a mixture of 60 milliliters (ml) of water, 3 ml of 49% HF, and 2 ml of 70%  $\text{HNO}_3$ ] of the phosphorus-doped  $\text{SiO}_2$  films was significantly faster than that of  
25 pure  $\text{SiO}_2$ , yielding values of 200Å/second, which concur with values of phosphorus-doped films produced by known chemical vapor deposition techniques previously discussed. The amount of dopant contained in the dielectric layer deposited by the above-described process may be  
30 controlled by adjusting the amount of dopant-containing precursor which is added to the reactant gas mixture.

Although phosphorus-doped  $\text{SiO}_2$  layers were formed as described above, it is also possible to form  
phosphorus-doped  $\text{SiO}$  layers by this process embodiment  
35 of the present invention by increasing the ratio of  $\text{SiH}_4$  to  $\text{N}_2\text{O}$  in a manner similar to that described in Example 1.

1       The photochemically deposited phosphorus-doped  
SiO<sub>2</sub> films formed by the above-described process of the  
present invention have application as dielectric layers  
for the passivation of charge-sensitive microelectronic  
5       devices, such as silicon MOS devices. In addition, these  
phosphorus-doped films may be used as a counter-diffusion  
layer on GaAs devices for the minimization of out-  
diffusion of both gallium (Ga) and arsenic (As) at tempera-  
tures exceeding 100°C.

### 10                   EXAMPLE 3

This example illustrates the use of the process  
in accordance with the third embodiment of the present  
invention as previously described herein.

15       Using the apparatus shown in FIG. 2 with two  
reactant gas chambers, a layer of SiO<sub>2</sub> was deposited on  
the surface of a wafer of silicon having a two-inch  
diameter. The general procedure described in relation  
to Example 1 above was followed, except that mercury  
20       sensitization was not used. A continuous flow photo-  
chemical reactor system was used. The oxygen-containing  
precursor was N<sub>2</sub>O and the selected vapor phase reactant  
was SiH<sub>4</sub>. Radiation having a wavelength of 1849Å  
was used to dissociate the N<sub>2</sub>O; and the window of the  
25       reaction chamber was formed of "spectrasil" (obtained  
from Thermal American Fused Quartz, Montville, New  
Jersey), which was transparent to 1849Å radiation. Low  
pressure mercury arc lamps designed with "spectrasil" en-  
velopes emitted radiation at 1849Å, which was transmitted  
30       through the "spectrasil" window into the reaction chamber.  
The radiation was absorbed by the N<sub>2</sub>O and caused dissocia-  
tion thereof to produce atomic oxygen. The atomic oxygen  
then reacted with the SiH<sub>4</sub> to produce the desired SiO<sub>2</sub>  
which deposited as a layer on the silicon wafer. A  
35       reactant gas flow ratio of SiH<sub>4</sub> to N<sub>2</sub>O of 2 sccm to 60  
sccm and an operating pressure of 3.7 Torr were used. The

1      $\text{SiO}_2$  layer was deposited at the rate of  $700\text{\AA}$  in 30 minutes, and even higher rates may be achieved with process optimization.

5             The refractive index of the photodeposited  $\text{SiO}_2$  layer formed by the above-described process of the present invention was determined by ellipsometry and the films were found to have a refractive index characteristic of  $\text{SiO}_2$ , i.e. 1.45. The etch rate characteristics of the photodeposited  $\text{SiO}_2$  material in  
10 buffered HF were comparable to those of  $\text{SiO}_2$  films deposited by low temperature plasma techniques.

           Although  $\text{SiO}_2$  layers were formed as described above, it is also possible to form  $\text{SiO}$  layers by this process embodiment of the present invention by increasing  
15 the ratio of  $\text{SiH}_4$  to  $\text{N}_2\text{O}$  in a manner similar to that described in Example 1.

           The photochemically deposited  $\text{SiO}_2$  layers formed by the above-described process of the present invention have application as dielectric layers for the passivation  
20 of semiconductor devices, particularly charge sensitive microelectronic devices, such as MOS devices and GaAs, HgCdTe photoconductive and photovoltaic devices, field-effect transistors. In addition, the oxide layers formed by the above-described process may be used on electro-  
25 optical materials such as lenses and mirrors or on solar cells as described in relation to Example 1.

           Using the above-described process,  $\text{SiO}_2$  layers were similarly deposited on Ge, InSb, and Al substrates.

           Furthermore, using the general process described  
30 above, a layer of  $\text{SiO}_2$  was deposited on the surface of a silicon wafer, using molecular oxygen ( $\text{O}_2$ ) as the oxygen-containing precursor. In order to completely inhibit the spontaneous thermal oxidation reaction of  $\text{O}_2$  and  $\text{SiH}_4$ , a nitrogen gas diluent was used and the pressure  
35 and flow rate conditions of the reactant gases were carefully controlled. Using an operating pressure of 0-5 Torr

- 1 and a reactant gas flow ratio of  $\text{SiH}_4/\text{O}_2/\text{N}_2$  of 1/20/80  
sccm, a layer of  $\text{SiO}_2$  was deposited at the rate of 3000  
to 4000 Å in 30 minutes. Thus, it may be seen that the  
use of molecular oxygen as the oxygen-containing precursor  
5 in practicing the present invention greatly enhances the  
oxide deposition rate.

#### EXAMPLE 4

- This example illustrates the use of the process  
10 in accordance with the fourth embodiment of the present  
invention as previously described herein.

- Using the apparatus described and illustrated in  
relation to FIG. 2 with three reactant gas chambers, a  
phosphorus-doped  $\text{SiO}_2$  layer was deposited on the surface  
15 of a silicon wafer having a two-inch diameter. The gene-  
ral procedure described in relation to Example 3 above  
was followed, with the addition of a third reactant gas.  
A continuous flow photochemical reactor system was used.  
Nitrous oxide was used as the oxygen-containing precursor,  
20 silane was the selected vapor phase reactant, and phos-  
phine was the dopant-containing precursor. Radiation  
having a wavelength of 1849 Å was used to dissociate  
the  $\text{N}_2\text{O}$  and the window of the reaction chamber was formed  
of "spectrasil" as discussed in relation to Example 3.  
25 The 1849 Å radiation was absorbed by the  $\text{N}_2\text{O}$  and caused  
dissociation thereof to produce atomic oxygen. The atomic  
oxygen then reacted with the  $\text{SiH}_4$  and  $\text{PH}_3$  as shown in  
Equation (18) above, to produce the desired phosphorus-  
doped  $\text{SiO}_2$ , which deposited as a layer on the silicon  
30 wafer. A low pressure continuous flow photochemical  
reactor system was used with a reactant gas flow ratio of  
 $\text{SiH}_4/\text{N}_2\text{O}/\text{PH}_3$  of 2/60/4 sccm. The  $\text{SiO}_2$  was deposited at  
the rate of 330 Å in 30 minutes, and even higher rates may  
be achieved with process optimization. The phosphorus-  
35 content of the deposited layer was approximately 5%.

1           The refractive index of the photodeposited phosphorus-doped  $\text{SiO}_2$  layer formed as described above was 1.75. The chemical composition of the deposited film was determined by Auger electron spectroscopy to be  
5           the value discussed above. The etch rate in "P-etch" [i.e., a mixture of 60 ml of water, 30 ml of 49% HF, and 2 ml of 70%  $\text{HNO}_3$ ] of the phosphorus-doped  $\text{SiO}_2$  film was determined to be significantly faster than that  
10           of pure  $\text{SiO}_2$ , having values comparable to phosphorus-doped films produced by known chemical vapor deposition techniques previously discussed.

          The photochemically deposited phosphorus-doped  $\text{SiO}_2$  films formed by the above-described process of the present invention find utility as discussed in relation  
15           to Example 2.

          While the present invention has been particularly described with the respect to the preferred embodiments thereof, it will be recognized by those skilled in the art that certain modifications in form and detail may be  
20           made without departing from the spirit and scope of the invention. In particular, the scope of the invention is not limited to the photochemical vapor deposition of silicon oxides, but is intended to include the photochemical vapor deposition of an oxide of any gas  
25           phase reactant that will react with atomic oxygen, such as reactants containing germanium, gallium, boron, indium, aluminum, titanium, tungsten and hafnium. In addition, the chemically unreactive oxygen-containing precursor is not limited to nitrous oxide, molecular oxygen, or nitrogen  
30           dioxide, but is intended to include any material which will photochemically dissociate to atomic oxygen, either with or without mercury sensitization. Further, the substrate on which oxide deposition may be performed by the process of the present invention is not limited to  
35           silicon, which was used merely as an example, but may include other semiconductor substrate materials, such as

1 GaAs, HgCdTe, or InSb, or electro-optical materials, such  
as lenses or mirrors, or GaAs or Si solar cells. Finally,  
the scope of the invention is not limited to the use of  
phosphine to produce phosphorus-doping, but is intended  
5 to include any dopant-containing precursor which is  
capable of mercury photosensitized dissociation to form  
neutral particles or which is capable of simultaneous  
oxidation by atomic oxygen with the selected gas reactant.  
Such precursors include diborane, arsine, stibine, hydrogen  
10 selenide, hydrogen sulfide, or hydrogen telluride, to  
produce boron-, arsenic-, antimony-, selenium-, sulfur-,  
or tellurium-doping, respectively.

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CLAIMS

1. A process for forming a layer of an oxide of a chosen material on the surface of a selected substrate, comprising the steps of exposing the substrate to a vapor-phase reactant and an oxygen-containing precursor in the presence of radiation of a predetermined wavelength to photochemically generate neutral oxygen atoms which react with the vapor-phase reactant to form said oxide layer under selected temperature, pressure and flow rate conditions.
2. A process according to claim 1, wherein said vapor-phase reactant contains silicon, germanium, gallium, boron, indium, aluminum, titanium, tungsten, or hafnium.
3. A process according to claim 2, wherein said vapor-phase reactant is silane ( $\text{SiH}_4$ ) and said oxide is silicon dioxide and/or silicon monoxide.
4. A process according to any preceding claim, wherein said oxygen-containing precursor is nitrous oxide ( $\text{N}_2\text{O}$ ), nitrogen dioxide ( $\text{NO}_2$ ), or molecular oxygen ( $\text{O}_2$ ).
5. A process according to any preceding claim, wherein the oxide layer is formed in the presence of photochemically generated dopant atoms to incorporate the dopant atoms into said oxide.
6. A process according to any preceding claim, wherein mercury vapor is added to said reactant and said precursor to cause mercury photosensitized dissociation of a chosen oxygen-containing precursor.
7. A process according to claim 6, wherein the oxygen-containing precursor is nitrous oxide ( $\text{N}_2\text{O}$ ), the vapor-phase reactant is silane ( $\text{SiH}_4$ ), the process is performed in a static photochemical reactor whereby the gas ratio of  $\text{SiH}_4$  to  $\text{N}_2\text{O}$  is 3 to 12 millimeters, and the temperature at which the process is maintained is 30 to 200°C.

8. A process according to claim 6, wherein the oxygen-containing precursor is nitrous oxide ( $N_2O$ ), the vapor-phase reactant is silane ( $SiH_4$ ), the process is performed in a continuous flow photochemical reactor whereby the gas flow ratio of  $SiH_4$  to  $N_2O$  is 2 to 10 standard cubic centimeters per minute (sccm), and the temperature at which the process is maintained is 30 to 200°C.

9. A process according to any of the claims 1-5, wherein the oxygen-containing precursor is nitrous oxide ( $N_2O$ ), the vapor-phase reactant is silane ( $SiH_4$ ), the predetermined wavelength is 1750 to 1950Å, the gas flow ratio of  $SiH_4$  to ~~oxygen~~  $N_2O$  is 2 to 60 standard cubic centimeters per minute, the temperature at which the process is maintained is 30 to 200°C, and the oxide is silicon dioxide ( $SiO_2$ ).

10. A process according to any of the claims 1-5, wherein the oxygen-containing precursor is molecular oxygen ( $O_2$ ) and nitrogen ( $N_2$ ) is admixed thereto, said predetermined wavelength is 1849Å, the vapor-phase reactant is silane ( $SiH_4$ ), said pressure is 0 to 5 Torr, and the gas flow ratio of  $SiH_4$  to  $O_2$  to  $N_2$  is 1 to 20 to 80 standard cubic centimeters per minute.

11. A process according to claim 5 or 6, wherein there is provided a dopant-containing precursor which is phosphine ( $PH_3$ ), diborane ( $B_2H_6$ ), arsine ( $AsH_3$ ), stibine ( $SbH_3$ ), hydrogen selenide ( $H_2Se$ ), hydrogen sulfide ( $H_2S$ ), or hydrogen telluride ( $H_2Te$ ).

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Fig. 1

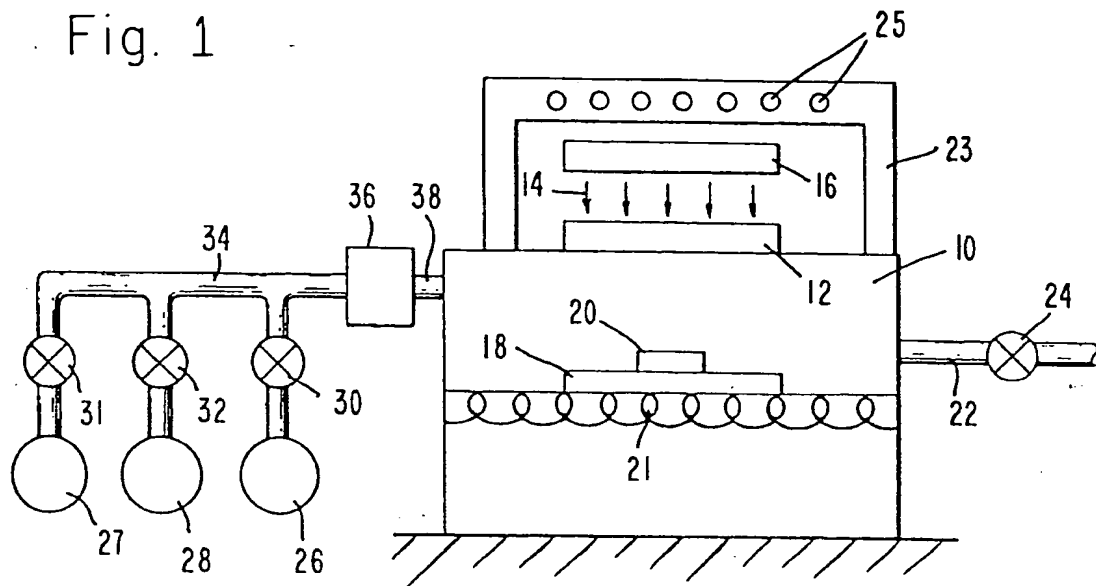
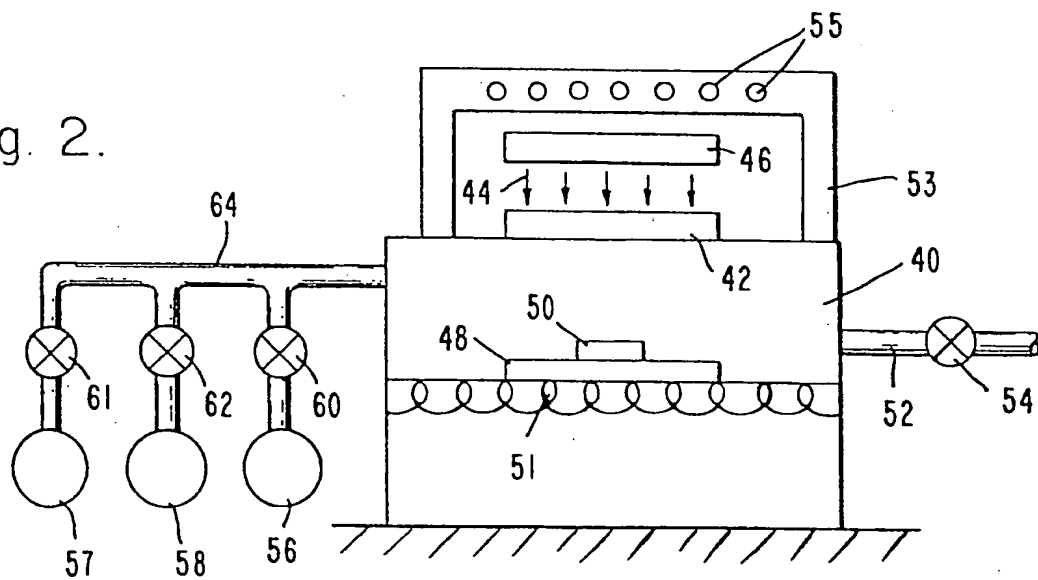


Fig. 2.





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# EUROPEAN SEARCH REPORT

0030798

Application number  
EP 80304143.3

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<p><u>DE - A - 1 564 963</u> (TEXAS)</p> <p>+ Totality +</p> <p>--</p> <p><u>AT - B - 287 789</u> (N.V. PHILIPS)</p> <p>+ Totality; especially claims 1,2,4,6 +</p> <p>--</p>		<p>H 01 L 21/205</p> <p>H 01 L 21/225</p> <p>H 01 L 21/268/</p> <p>H 01 L 21/316</p> <p>H 01 L 21/365</p> <p>H 01 L 21/385</p> <p>H 01 L 21/428</p>
A	<p><u>DE - B - 1 444 520</u> (RCA)</p> <p>+ Totality; especially column 2, line 63 - column 4, line 8; claims 1,2 +</p> <p>--</p>		<p>TECHNICAL FIELDS SEARCHED (Int. Cl. 7)</p>
A	<p><u>US - A - 3 767 484</u> (TAKAGI)</p> <p>+ Totality; especially column 3, line 68 - column 4, line 3 +</p> <p>--</p>		<p>B 41 N</p> <p>G 03 F</p> <p>H 01 L</p>
A	<p><u>US - A - 3 907 616</u> (WIEMER)</p> <p>+ Totality; especially column 6, line 49 - column 7, line 10; claims 1,5,7,8 +</p> <p>--</p>		
	<p><u>US - A - 3 769 104</u> (ONO)</p> <p>+ Totality; especially column 2, line 67 - column 3, line 21 +</p> <p>--</p>		
D,A	<p>JOURNAL OF VACUUM SCIENCE &amp; TECHNOLOGIE, Vol. 14, No. 5, Sept./Oct. 1977</p> <p>KERN-ROSIER "Advances in deposition process for passivation films", pages 1082-1099</p> <p>+ Totality +</p> <p>--</p>		<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant</p> <p>A: technological background</p> <p>O: non-written disclosure</p> <p>P: intermediate document</p> <p>T: theory or principle underlying the invention</p> <p>E: conflicting application</p> <p>D: document cited in the application</p> <p>L: citation for other reasons</p>
X	The present search report has been drawn up for all claims		<p>&amp;: member of the same patent family.</p> <p>corresponding document</p>
Place of search		Date of completion of the search	Examiner
VIENNA		19-02-1981	FRANZ



European Patent  
Office

## EUROPEAN SEARCH REPORT

0030798

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>3</sup> )
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D, A	JOURNAL OF VACUUM SCIENCE & TECHNOLOGIE, Vol 14, No. 5, Sept./Oct. 1977  AMICK-SCHNABLE-VOSSEN "Deposition techniques for dielectric films on semiconductor devices", pages 1053-1063  + Totality +		
			TECHNICAL FIELDS SEARCHED (Int. Cl. <sup>3</sup> )